Shrinking rate of polymer gels composed of star-shaped polymers of N-isopropylacrylamide and dimethylacrylamide copolymers: effect of dimethylacrylamide into the crosslinking network

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Experiment

1. Materials

1.1 Purification of NIPA

In a 500 mL triangular flask, 100 g of NIPA, 25 mL of toluene, and 75 mL of hexane were added and warmed to 60 °C in a water bath to completely dissolve the NIPA. After allowing the mixture to stand until it reached room temperature, a rubber stopper was placed over the triangular flask and the flask was allowed to stand for 2 days. The solid sample that precipitated was filtered by suction while washing with hexane cooled in ice water. The same recrystallization procedure was repeated for the solid sample obtained, and the sample was dried in a bell jar vacuum oven at 40 °C for 1 day. The above operations yielded 88.9 g (88.9 % yield) of purified NIPA.

1.2 Purification of CuCl

First, 3 N HCl was prepared by mixing 20 mL of 12 N HCl with 60 mL of ultrapure water. Further, 3.3×10^{-3} N HCl was prepared by mixing 0.5 mL of 3 N HCl with 450 mL of ultrapure water. To a 100 mL triangular flask containing 3 g of copper chloride, 75 mL of 3 N hydrochloric acid was added and stirred with a magnetic stirrer to dissolve all the copper chloride in solution. In a 500 mL triangular flask, 450 mL of ultrapure water was added, stirred with a magnetic stirrer, and the copper chloride mixture was added drop by drop. After the drop was completed, stirring was continued for 20 minutes, and then the stirring was stopped and allowed to stand for 10 minutes to allow the copper chloride to settle. After removing the supernatant with a dropper, 3.3×10^{-3} N hydrochloric acid was added and stirred again for 20 minutes, and then left for 10 minutes to allow the copper chloride to settle. This operation was repeated a total of three times. The precipitated compound was filtered by suction and washed with 3.3×10^{-3} N hydrochloric acid, methanol, and diethyl ether in that order. The resulting white solid was vacuum dried in a bell jar vacuum oven at 50 °C for 24 hours.

2. Synthesis

2.1 Synthesis of tetrabranched PNIPA

28.5 mg (0.288 mmol) of CuCl and 77.0 μL (0.288 mmol) of Me₆TREN were placed in a nitrogen-replenished 100 mL flask, 1.92 mL of water was added, and the catalyst was stirred for 1 hour. Next, a monomer solution was prepared by placing 3.26×10^{3} mg (28.8 mmol) of NIPA and 35.9 mg (0.072 mmol) of PETCP in a nitrogen-replaced 200 mL flask and adding 8.17 mL of water and 10.1 mL of DMF. The monomer solution was added to the complex solution and stirred at 4 °C for 1 h with argon flow. The concentration of NIPA in the final reaction system was 1.2 mol L⁻¹ and the molar ratio of the reagents was [NIPA] : [PETCP] : [CuCl] : [Me₆TREN] = 400 : 1 : 4 : 4. The reaction was stopped by collecting the reaction solution with a syringe and adding solvent during

the reaction. This was used as a sample for the evaluation of the reaction over time. The sampled solution was diluted with THF and passed through a silica gel column to remove the copper complex. The solvent was removed from the solution after catalyst removal using a convenience evaporator. The sample was then dissolved in the eluent for SEC measurement (LiBr dissolved in DMF at a concentration of 5 mmol L^{-1}) to achieve a sample concentration of 2 wt%, and this solution was filtered through a membrane filter Millex-LCR SLCRX13NL 13 mm (pore size 0.45 μm) before SEC measurement. Molecular weight and molecular weight distribution were calculated using a calibration curve prepared from the SEC results of polystyrene standards.

2.2 Synthesis of tetrabranched PNIPA$_{0.8}$-b-PDMA$_{0.2}$

A tetrabranched block copolymer (PNIPA$_{0.8}$-b-PDMA$_{0.2}$) with a composition ratio of PNIPA: PDMA = 0.8 : 0.2 was synthesized. 28.51 mg (0.288 mmol) of CuCl and 77.0 μL (0.288 mmol) of Me$_6$TREN were placed in a nitrogen-replenished flask, 0.92 mL of water was added and stirred for 1 hour to disproportionate the catalyst. Next, 2.61 x 10^3 mg (23.1 mmol) of NIPA and 35.9 mg (0.072 mmol) of PETCP were placed in a 200 mL flask with nitrogen replacement, and 7.14 mL of water and 8.06 mL of DMF were added to dissolve the NIPA solution; in a 50 mL flask also with nitrogen replacement, DMA 0.59 mL (mmol) of DMA monomer solution was prepared by adding 2.10 mL of water and 2.10 mL of DMF. The NIPA monomer solution was added to the complex solution and stirred at 4 °C for 1 hour with argon flow. The DMA solution was then added and stirred for 30 min. The reaction was stopped by collecting the reaction solution with a syringe and adding solvent during the reaction. This was used as a sample for the evaluation of the change over time of the reaction. The sampled solution was diluted with THF and passed through a silica gel column to remove the copper complex. The solvent was removed from the solution after catalyst removal using a convenience evaporator. The sample was then dissolved in eluent for SEC measurement at a sample concentration of 2 wt%, and the solution was filtered through a membrane filter Millex-LCR SLCRX13NL 13 mm (pore size 0.45 μm) before SEC measurement. Molecular weight and molecular weight distribution were calculated using a calibration curve prepared from the SEC results of polystyrene standards.

2.3 Synthesis of spherical gels composed of branched PNIPA

226.3 mg of NIPA and 2.49 mg of tetrabranched initiator were placed in a test tube and placed in a glove box with nitrogen replacement. Inside the glove box, 0.23 mL of ultrapure water and 0.62 mL of DMF, which were replaced with argon gas, were added and stirred at room temperature to dissolve to make a monomer solution. Also, 3.96 mg of CuCl was placed in another test tube and placed in a glove box with nitrogen replacement. 0.39 mL of ultrapure water and 10.69 μL of Me$_6$TREN, which were replaced with argon gas in the glove box, were stirred (about 300 rpm) at 4°C for 1 hour to make a catalyst solution. Then, 1.1 mL of monomer solution was added to the catalyst solution to initiate polymerization. At this time, the monomer concentration in the reaction solution was 1.33 mol L^{-1}, the volume ratio of water to DMF was 1 : 1, and the substance ratio was CuCl:Me$_6$TREN:NIPA:initiator = 1:1:400:1. In addition, 30.8 mg of MBAA was placed in another

test tube and placed in a glove box. Inside the glove box, 1.60 mL of ultrapure water and 0.86 mL of DMF, which were replaced with argon gas, were added and stirred at room temperature to dissolve to make a crosslinker solution. One hour after the start of polymerization, 2.50 mL of the crosslinker solution was added to initiate crosslinking. The final crosslinker concentration in the reaction solution was 50 mmol L^{-1}, the monomer concentration was 0.50 mol L^{-1}, and the volume ratio of water to DMF was 6 : 4. The solution was stirred at about 800 rpm for 1 minute and 20 seconds, then dropped by Pasteur pipette into a solution of silicone oil (KF-96L-2cs + DOWSIL™ RSN-0749 Resin12 3 wt%) (hereinafter referred to as the oil phase) that had been replaced with argon gas and cooled to 4°C. The mixture was stirred for 1 hour at about 1000 rpm. The particle size of the gel particles was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) and the average particle size was calculated. The resulting gel particles were washed with hexane, methanol, and water, in that order, to obtain spherical gels dispersed in water. In washing, the spherical gel in the test tube was allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added in a series of repeated operations. The gel in its dispersed state in water was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) to calculate the average particle size.

2.4 Synthesis of spherical gels composed of tetrabranched PNIPA$_{1-x}$-b-PDMA$_x$

Spherical gels consisting of a tetrabranched block copolymer (PNIPA$_{1-x}$-b-PDMA$_x$) with a composition ratio of PNIPA:PDMA = 1-x : x (x = 0.1, 0.2, 0.3) were synthesized.

(i) x = 0.1

203.7 mg of NIPA and 2.49 mg of tetrabranched initiator were placed in a test tube and placed in a glove box with nitrogen replacement. In the glove box, 0.44 mL of ultrapure water and 0.63 mL of DMF, both replaced with argon gas, were added and stirred at room temperature to dissolve to make a NIPA monomer solution. In another test tube in the glove box, 20.65 μL of argon-substituted DMA, 73.00 μL of ultrapure water, and 73.00 μL of DMF were placed and stirred at room temperature to make a DMA monomer solution. Also, 1.98 mg of CuCl was placed in another test tube and placed in a glove box with nitrogen replacement. 0.19 mL of ultrapure water and 5.35 μL of Me$_6$TREN, which were replaced with argon gas in the glove box, were stirred at 4°C for 1 hour (about 300 rpm) to make a catalyst solution. To the catalyst solution, 1.30 mL of NIPA monomer solution was added to initiate polymerization, and after 1 hour, 0.17 mL of DMA monomer solution was added. At this time, the monomer concentration in the reaction solution was 1.33 mol L^{-1}, the volume ratio of water to DMF was 1 : 1, and the substance ratio was CuCl:Me$_6$TREN:NIPA+DMA:initiator = 1 : 1 : 400 : 1. Another 30.83 mg of MBAA was placed in another test tube and placed in a glove box. Inside the glove box, 1.52 mL of ultrapure water and 0.78 mL of DMF, which were replaced with argon gas, were added and stirred at room temperature to dissolve to make the crosslinker solution. Thirty minutes after the addition of the DMA monomer solution, 2.33 mL of the crosslinker solution was added to initiate crosslinking. The final crosslinker concentration in the reaction solution was 50 mmol L^{-1}, the monomer concentration was

0.50 mol L^{-1}, and the volume ratio of water to DMF was 6 : 4. After stirring at about 800 rpm for 1 minute and 20 seconds, the solution was dropped with a Pasteur pipette into the oil phase, which had been replaced with argon gas and cooled to 4°C. The solution was stirred at about 1000 rpm for 1 hour. The particle size of the gel particles was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) and the average particle size was calculated. The resulting gel particles were washed with hexane, methanol, and water, in that order, to obtain spherical gels dispersed in water. In washing, the spherical gel in the test tube was allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added in a series of repeated operations. The gel in its dispersed state in water was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) to calculate the average particle size.

(ii) x = 0.2

181.05 mg of NIPA and 2.49 mg of tetrabranched initiator were placed in a test tube and placed in a glove box with nitrogen replacement. In the glove box, 0.37 mL of ultrapure water and 0.56 mL of DMF, both replaced with argon gas, were added and stirred at room temperature to dissolve to make a NIPA monomer solution. In another test tube in the glove box, 41.30 μL of argon-substituted DMA, 0.15 mL of ultrapure water, and 0.15 mL of DMF were placed and stirred at room temperature to make a DMA monomer solution. Also, 1.98 mg of CuCl was placed in another test tube and placed in a glove box with nitrogen replacement. 0.19 mL of ultrapure water and 5.35 μL of Me$_6$TREN, which were replaced with argon gas in the glove box, were stirred at 4°C for 1 hour (about 300 rpm) to make a catalyst solution. To the catalyst solution, 1.13 mL of NIPA monomer solution was added to initiate polymerization, and after 1 hour, 0.33 mL of DMA monomer solution was added. At this time, the monomer concentration in the reaction solution was 1.33 mol L^{-1}, the volume ratio of water to DMF was 1 : 1, and the substance ratio was CuCl:Me$_6$TREN:NIPA+DMA:initiator = 1 : 1 : 400 : 1. Another 30.83 mg of MBAA was placed in another test tube and placed in a glove box. Inside the glove box, 1.52 mL of ultrapure water and 0.78 mL of DMF, which were replaced with argon gas, were added and stirred at room temperature to dissolve to make the crosslinker solution. Thirty minutes after the addition of the DMA monomer solution, 2.33 mL of the crosslinker solution was added to initiate crosslinking. The final crosslinker concentration in the reaction solution was 50 mmol L^{-1}, the monomer concentration was 0.50 mol L^{-1}, and the volume ratio of water to DMF was 6 : 4. After stirring at about 800 rpm for 1 minute and 20 seconds, the solution was dropped with a Pasteur pipette into the oil phase, which had been replaced with argon gas and cooled to 4 °C. The solution was stirred at about 1000 rpm for 1 hour. The particle size of the gel particles was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) and the average particle size was calculated. The resulting gel particles were washed with hexane, methanol, and water, in that order, to obtain spherical gels dispersed in water. In washing, the spherical gel in the test tube was allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added in a series of repeated operations. The gel in its dispersed state in water was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) to calculate the average particle size.

(iii) x = 0.3

158.42 mg of NIPA and 2.49 mg of tetrabranched initiator were placed in a test tube and placed in a glove box with nitrogen replacement. In the glove box, 0.29 mL of ultrapure water and 0.49 mL of DMF, both replaced with argon gas, were added and stirred at room temperature to dissolve to make a NIPA monomer solution. In another test tube in the glove box, 61.96 μL of argon-substituted DMA, 0.22 mL of ultrapure water, and 0.22 mL of DMF were placed and stirred at room temperature to make a DMA monomer solution. Also, 1.98 mg of CuCl was placed in another test tube and placed in a glove box with nitrogen replacement. 0.19 mL of ultrapure water and 5.35 μL of Me$_6$TREN, which were replaced with argon gas in the glove box, were stirred at 4°C for 1 hour (about 300 rpm) to make a catalyst solution. To the catalyst solution, 0.97 mL of NIPA monomer solution was added to initiate polymerization, and after 1 hour, 0.5 mL of DMA monomer solution was added. At this time, the monomer concentration in the reaction solution was 1.33 mol L^{-1}, the volume ratio of water to DMF was 1 : 1, and the substance ratio was CuCl:Me$_6$TREN:NIPA+DMA:initiator = 1 : 1 : 400 : 1. Another 30.83 mg of MBAA was placed in another test tube and placed in a glove box. Inside the glove box, 1.52 mL of ultrapure water and 0.78 mL of DMF, which were replaced with argon gas, were added and stirred at room temperature to dissolve to make the crosslinker solution. Thirty minutes after the addition of the DMA monomer solution, 2.33 mL of the crosslinker solution was added to initiate crosslinking. The final crosslinker concentration in the reaction solution was 50 mmol L^{-1}, the monomer concentration was 0.50 mol L^{-1}, and the volume ratio of water to DMF was 6 : 4. After stirring at about 800 rpm for 1 minute and 20 seconds, the solution was dropped with a Pasteur pipette into the oil phase, which had been replaced with argon gas and cooled to 4 °C.   The solution was stirred at about 1000 rpm for 1 hour. The particle size of the gel particles was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) and the average particle size was calculated. The resulting gel particles were washed with hexane, methanol, and water, in that order, to obtain spherical gels dispersed in water. In washing, the spherical gel in the test tube was allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added in a series of repeated operations. The gel in its dispersed state in water was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) to calculate the average particle size.

2.5 Synthesis of spherical gels composed of tetrabranched PNIPA$_{0.8}$-r-PDMA$_{0.2}$

Spherical gels consisting of a tetrabranched random copolymer (tetrabranched PNIPA$_{0.8}$-r-PDMA$_{0.2}$) with a composition ratio of PNIPA: PDMA = 0.8 : 0.2 were synthesized. 181.06 mg of NIPA and 2.49 mg of tetrabranched initiator were placed in a test tube and placed in a glove box with nitrogen replacement. In the glove box, 41.31 μL of DMA, 0.511 mL of ultrapure water, and 0.706 mL of DMF, all replaced with argon gas, were stirred and dissolved at room temperature to make a monomer solution. Also, 1.98 mg of CuCl was placed in another test tube and placed in a glove box with nitrogen replacement. 0.19 mL of ultrapure water and 5.35 μL of Me$_6$TREN, which were replaced with argon gas in the glove box, were stirred (about 300 rpm) at 4°C for 1 hour to

make a catalyst solution. Polymerization was initiated by adding 1.47 mL of monomer solution to the catalyst solution. The monomer concentration in the reaction solution was 1.33 mol L^{-1}, the volume ratio of DMF to water was 1:1, and the substance ratio was $CuCl:Me_6TREN:NIPA+DMA:initiator = 1:1:400:1$. Another 30.83 mg of MBAA was placed in another test tube and placed in a glove box. Inside the glove box, 1.52 mL of ultrapure water and 0.78 mL of DMF, which were replaced with argon gas, were added and stirred at room temperature to dissolve to make a crosslinker solution. One hour after the polymerization was started, 2.33 mL of the crosslinker solution was added to initiate crosslinking. The final crosslinker concentration in the reaction solution was 50 mmol L^{-1}, the monomer concentration was 0.50 mol L^{-1}, and the volume ratio of water to DMF was 6 : 4. After stirring at about 800 rpm for 1 minute and 20 seconds, the solution was dropped with a Pasteur pipette into the oil phase, which had been replaced with argon gas and cooled to 4 °C. The solution was stirred at about 1000 rpm for 1 hour. The particle size of the gel particles was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) and the average particle size was calculated. The resulting gel particles were washed with hexane, methanol, and water, in that order, to obtain spherical gels dispersed in water. In washing, the spherical gel in the test tube was allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added in a series of repeated operations. The gel in its dispersed state in water was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) to calculate the average particle size.

2.6 Synthesis of spherical gels by free radical polymerization

226.32 mg of NIPA and 12.33 mg of MBAA were placed in a test tube, and 1.14 mg of APS in another test tube. These were placed in a glove box with nitrogen replacement. A mixture of ultrapure water and DMF (volume ratio 6 : 4) with argon gas replacement was prepared in the glove box. 2.79 mL of the water/DMF mixture was placed in a test tube containing NIPA and MBAA to make the prepared solution. To a test tube containing APS, 0.93 mL of water/DMF mixed solvent was added to make the initiator solution. After stirring at 4°C for 30 minutes, the prepared solution was added to the initiator solution to initiate the reaction. The final concentration of crosslinker in the reaction solution was 20 mmol L^{-1} and the volume ratio of water to DMF was 6 : 4. Five minutes after the start of the reaction, 3.37 μL of TEMED was added. After stirring at about 800 rpm for 1 minute and 20 seconds, the mixture was dropped by Pasteur pipette into the oil phase, which had been replaced with argon gas and cooled to 4°C. The particle size of the gel particles was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) and the average particle size was calculated. The resulting gel particles were washed with hexane, methanol, and water, in that order, to obtain spherical gels dispersed in water. In washing, the spherical gel in the test tube was allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added in a series of repeated operations. The gel in its dispersed state in water was measured by DISITAL MICROSCOPE VHX-500K (EYENCE) to calculate the average particle size.

3. Results and Discussion

3.1 Synthesis of tetrabranched PNIPA

^{1}H NMR spectra of the monomer solution (0 min) and the reaction solution sampled after 1 h are shown in Figure S1. The hydrogen peak of the vinyl group of NIPA disappeared 1 hour after the reaction started. The integral ratio of the vinyl group hydrogen peak of NIPA (5.5 ppm) was normalized by the aldehyde hydrogen peak of DMF (8.0 ppm), and the monomer conversion was calculated from the following equation to give a conversion ratio of approximately 95%.

Conversion rate (%) = $(1-I_t/I_0)\times100$

I_0 : Normalized integral ratio of vinyl group hydrogen of NIPA in monomer solution
I_t : Normalized integral ratio of vinyl group hydrogen of NIPA in the polymerized solution at reaction time t

SEC measurement results are shown in Figure S2. The calculated average molecular weight and molecular weight distribution are plotted against reaction time (Figure S3). The average molecular weight of PNIPA at a reaction time of 1 hour, when the reaction was almost complete, was 5.0×10^4. The molecular weight distribution was about 1.1. The number-average molecular weight calculated from the SEC measurement was plotted against the monomer conversion (Figure S4). The average molecular weight increased linearly as the reaction proceeded. This indicates that the polymerization system is living, with few stopping reactions such as recombination and disproportionation.

3.2 Synthesis of branched PNIPA$_{0.8}$-b-PDMA$_{0.2}$

In the polymerization reaction of NIPA, the average molecular weight and molecular weight distribution calculated from SEC measurements were plotted against reaction time (Figure S5). The average molecular weight and molecular weight distribution of PNIPA were 4.0×10^4 and 1.06, respectively, for a reaction time of 1 hour, when the polymerization reaction of NIPA was almost complete. The molecular weight calculated from the SEC measurement was plotted against the monomer conversion (Figure S6). The average molecular weight increased linearly as the reaction proceeded, indicating that the reaction was living with little stopping reaction.

☐Next, in the polymerization reaction of DMA, the ^{1}H NMR spectra of the DMA solution (0 min) and the reaction solution sampled 30 min after the addition of DMA are shown in Figure S7. The peak of hydrogen of the vinyl group of DMA disappeared 30 minutes after the addition of DMA. The integral ratio of the vinyl group hydrogen peak of DMA (6.7 ppm) was normalized by the aldehyde hydrogen peak of DMF (8.0 ppm), and the monomer conversion was calculated from the following formula to be about 95%.

Conversion rate (%) = $(1-I_t/I_0)\times100$

I_0 : Normalized integral ratio of vinyl group hydrogen of DMA in monomer solution

I_t : Normalized integral ratio of vinyl group hydrogen of DMA in polymerized solution at reaction time t

The results of SEC measurements immediately before the addition of DMA, i.e., 1 hour after the start of polymerization of NIPA, and 30 minutes after the start of polymerization of DMA are shown in Figure S8. The calculated number-average molecular weight and molecular weight distribution are plotted against reaction time (Figure S9). The molecular weight and molecular weight distribution of PNIPA$_{0.8}$-b-PDMA$_{0.2}$ 30 minutes after the addition of DMA were 4.5 x 10^4 and 1.06, respectively. The molecular weight calculated from SEC measurements was plotted against the monomer conversion (Figure S10). The average molecular weight increased linearly as the reaction proceeded. This indicates that the polymerization system is living, with few stopping reactions such as recombination and disproportionation.

3.3 Spherical gel particle size

Particle size was measured by digital microscope VHX-500K (EYENCE) and the average particle size was calculated. Particle size distributions of synthesized PNIPA gels, PNIPA$_{1-x}$-b-PDMA$_x$ (x = 0.1, 0.2, 0.3) gels, PNIPA$_{0.8}$-r-PDMA$_{0.2}$ gels and conventional gels by free radical polymerization are shown in Figures S11~S16. For each gel, (a) shows the frequency distribution of the gel in the oil phase as prepared, and (b) shows the frequency distribution of the gel in the equilibrium swollen state after being washed with hexane, methanol, and water and dispersed in water. For all gels, the particle size of about 300 particles was measured for both the prepared and equilibrium swollen gels. From Figure S11~Figure S16, it can be seen that all gels are on the order of several hundred micrometers and have a CV value of 20~50, which represents the monodispersibility of the particles.

CV[%]=(σ/D)×100 (σ: standard deviation, D: average particle size)

It is obtained by the following formula. In general, a CV value of 10% or less is considered to be highly monodisperse. The CV values of the prepared gels are extremely larger than 10%, which indicates that they are polydisperse. In all gels, the particle size distribution shifts to the right from the prepared state to the equilibrium swollen state, and the particles are swollen. However, comparing the particle size distribution in the prepared state with that in the equilibrium swollen state, it can be seen that the shape of the distribution is different. If all the gels in the prepared state swell to the ideal degree of swelling, the distribution should only shift to the right and not change shape from the prepared state to the equilibrium swollen state. There are two possible reasons for the change in the shape of the distribution in this case. First, the number of particles measured was small. It is said that the number of droplets in the same sample should be at least 1,000 to obtain statistically accurate information, and 300 particles were not enough for this measurement. Second, there was a lot of particle loss during the displacement of the gel from the oil phase to the aqueous

phase, which is the state of preparation. Washing was performed by repeating a series of operations six times for each solvent, in which the spherical gels in the test tubes were allowed to settle spontaneously, the supernatant was removed, and a new washing solution was added. During spontaneous sedimentation, the supernatant may have been removed despite the presence of particles that had not fully settled. Figure S17 shows the degree of swelling of each gel. The degree of swelling was calculated from the average particle size (d) of the gel in its equilibrium swollen state dispersed in water, relative to the average particle size (d_0) of the gel in the oil phase in its prepared state, using the following formula,

Swelling ratio = d/d_0

Figure S17 shows that there was no systematic change in the amount of DMA or copolymerization in each gel. This may be due to the large CV values and polydispersity of all gels and the different shape of the particle size distribution in the prepared and equilibrium swollen states, as described above, which do not accurately indicate the degree of swelling. In order to obtain accurate values of the degree of swelling, it is considered necessary to obtain more monodisperse particles or to synthesize the gels using cylinders of known inner diameter or the like in order to equalize the size of the prepared state in all gels.

The particle size changes of the synthesized PNIPA gels and $PNIPA_{1-x}$-b-$PDMA_x$ (x = 0.1, 0.2, 0.3) gels are shown in Figure S18 and Figure S19. Figure S18 shows the particle size of the gel in the oil phase as prepared, and Figure S19 shows the particle size of the gel in the equilibrium swollen state after washing with hexane, methanol, and water and dispersion in water. Figure S18 shows the particle size of gel in the oil phase, and Figure S19 shows the particle size of gel in the equilibrium swollen state after being washed with hexane, methanol, and water and dispersed in water. The particle size of the gel tends to decrease as the amount of DMA incorporated into the network structure increases. When mechanical stirring disperses one of the liquid phases from the water/oil interface into the other phase as a droplet and subdivides it, the droplet should be distorted as much as possible. It was derived from hydrodynamics by Taylor that the distortion of a dispersed droplet suspended in a dispersant under a constant shear rate gradient can be expressed by the following equation,

$$\frac{L-B}{L+B} = \frac{Ga\eta}{2\gamma} \times \frac{19p+16}{16p+16} \quad （1）$$

where L is the major axis diameter of an elliptically distorted dispersed droplet, B is its minor axis diameter, G is the shear rate, α is the diameter of this dispersed droplet when it is spherical, η is the viscosity of the dispersant, γ is the interfacial tension between the two liquid phases, and p is the viscosity ratio of the dispersed phase and dispersant. The closer the value on the left-hand side of equation (1) is to 1, the thinner and more elongated the droplet becomes, and the more easily small spheres are formed. This is achieved by a large shear rate gradient due to severe agitation, high

dispersant viscosity, and low interfacial tension. In this study, all gels were agitated at the same speed, so the shear rate gradient is equal and the oil phase, silicone oil and surfactant, is the same type. Therefore, the decrease in particle size due to the incorporation of DMA in the network structure can be attributed to the lower interfacial tension between the gelling solution and the oil phase.

3.4 Reactivity ratio of NIPA and DMA

When two monomers are randomly copolymerized, the monomer reactivity ratio is a measure of whether the terminal radicals are more likely to react with the same monomer or the other monomer. The monomer reactivity ratio varies with the combination of monomers. Here, the monomer reactivity ratios have been determined for PNIPA and PDMA prepared by RAFT polymerization, where $r_{NIPA} = 0.83$ and $r_{DMA} = 1.1054$. This indicates that NIPA is 1.32 times less reactive than DMA, which may be attributed to the bulky side chain of NIPA and steric hindrance between radicals. If the monomer reactivity ratios for the two monomers are r_1 and r_2, respectively, it means that polymerization of the homologous monomer occurs preferentially when $r_1 \times r_2 > 1$, and copolymerization does not proceed. Since $r_{NIPA} \times r_{DMA} = 0.917 < 1$, copolymerization is proceeding in the synthesis of $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel. However, since smaller values of $r_1 \times r_2$ indicate greater alternating copolymerization, the sequence of NIPA and DMA in the synthesized $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel is considered to be less random.

3.5 Calculation of collective diffusion coefficient (swelling)

Since the temperature jump from the initial temperature to near the attained temperature takes several seconds, the diameter change during this time must be truncated. Therefore, the time when the temperature reached near the attained temperature was calculated as t_i, and the diameter at that time was calculated as the initial diameter $d(t_i)$.

3.6 Change in t_1 in shrinkage behavior

In the temperature jump experiment, t_1 was defined as the time t_1 reached near the attained temperature and the time t_1 as the time t_1 switches between stage 1 and stage 2 in a contraction with phase separation. Here, t_1' is defined as $t_1' = t_1 - t_i$. Figure S71 shows the change in t_1' for each gel when the temperature jump test was performed with the initial temperature fixed at 20°C and the attained temperature varied. Since t_i is almost the same for all gels, we can say that t_1' represents the apparent change in t_1. It can be seen that t_1' decreases as the attained temperature increases for all gels. This can be attributed to the increase in driving force due to the increase in ΔT. The results show that in the high temperature region, t_1' is larger for $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel, $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel, and $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel compared to PNIPA gel and $PNIPA_{0.9}$-b-$PDMA_{0.1}$ gel. t_1 is considered to be the time when the gel enters the metastable or unstable region due to the temperature jump. Therefore, we can consider that the metastable and unstable regions change for $PNIPA_{0.8}$-b-$PDMA_{0.2}$ gel, $PNIPA_{0.7}$-b-$PDMA_{0.3}$ gel, and $PNIPA_{0.8}$-r-$PDMA_{0.2}$ gel.